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PCT

#3

TRANSMITTAL LETTER**PATENT**

Docket No. 108-C1553US

Commissioner for Patents
 Washington, D.C. 20231

Inventor(s): Dr. Peter KUHLMANN and Reinhard WINTER

Application No. 09/700,901

Group Art Unit: Unknown

Application Filing Date: 11/17/2000

Examiner: Unknown

International Application Filing Date: 05/19/98

Title: ALKYL RESIN EMULSIONS AND UTILIZATION OF THE SAME

- ☒ A Combined Declaration, Power of Attorney and Petition is attached.
- ☒ A copy of the Notification of Missing Requirements Under 35 U.S.C. 371 In The United States Designated/Elected Office (DO/EO/US)
- ☐ A Verified Statement to Establish Small Entity Status is attached.
- ☐ A Verified Statement to Establish Small Entity Status has already been filed in this application.
- ☐ Enclosed is/are _____ in the above-identified application.
- ☒ **Please charge to Deposit Account 50-1208 the missing requirements surcharge** and any other fees under 37 CFR 1.16 and 1.17 which may be required during the entire pendency of this application. This authorization includes the fee for any extension of time under 37 CFR 1.136(a) that may be necessary. To the extent any such extension should become necessary it is hereby requested.

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130.00 CH

Respectfully submitted,

Registration Number 29,524	Telephone Number 651.251.2250	Signature
Date 18 January 2001	Print Name David R. Cleveland	

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PATENT

Docket No.

108-C1553US

TRANSMITTAL OF PATENT APPLICATION -
TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

Box: Patent Application
Commissioner for Patents
Washington, D.C. 20231

Inventor(s): Peter KUHLMANN and Reinhard WINTER

Title: ALKYL RESIN EMULSIONS AND UTILIZATION OF THE SAME
International Application No.: WO 99/60044
International Filing Date: 19 May 1998
Priority Date Claimed: 19 May 1998

1. ☒ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
3. ☒ A Verification of Translation.
4. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
5. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
6. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
7. ☒ A Communication Regarding Substitute Specification and Substitute Specification.
8. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
9. ☐ An English translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
10. ☒ The application includes 0 sheet(s) of drawings.
11. ☒ The fee for filing the application is computed as follows:

Claims As Filed				
(1) For	(2) Number Filed	(3) Number Extra	(4) Rate	(5) Basic Fee* \$860.
Total Claims	10 -20 =	0	x \$18.	\$0
Independent Claims	1 -3 =	0	x \$80.	\$0
Additional fee for filing one or more multiple dependent claims			\$270.	\$0
Total amount due →				\$860

*International fee not paid to United States Patent and Trademark Office but International Search Report prepared by EPO or IPO

09/700901


526 Rec'd PCT/FTO 17 NOV 2000


**TRANSMITTAL OF PATENT APPLI
TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371 (Cont'd...)**

12. ☒ Enclosed is a check in the amount of \$860 for the filing fee.
13. ☒ Please charge to Deposit Account 501208 any fees under 37 CFR 1.16 and 1.17 which may be required for filing or otherwise during the entire pendency of this application. This authorization includes the fee for any extension of time under 37 CFR 1.136(a) that may be necessary. To the extent any such extension should become necessary it is hereby requested. A copy of this transmittal letter for fee processing is enclosed.
14. ☒ Enclosed is a return receipt postcard

Respectfully submitted,

Registration Number	Telephone Number
29,524	651.251.2250
Date 17 November 2000	

Signature 
Printed Name David R. Cleveland

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Express Mail Mailing Label No. EF285972778US	Signature of Person Mailing Application 
Date of Deposit November 17, 2000	Printed Name of Person Mailing Application David R. Cleveland

09/700901

525 Rec'd PCT. JTO 17 NOV 2000
Patent

Docket No.: 108-C1553US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:
Peter KUHLMANN and Reinhard
WINTER

Serial No.:
Filed: November 17, 2000
For: **ALKYD RESIN EMULSIONS
AND USES THEREOF**

Group Art Unit:

Examiner:

COMMUNICATION REGARDING SUBSTITUTE SPECIFICATION

Commissioner for Patents
Washington, D.C. 20231

Dear Sir:

Enclosed is a Substitute Specification for the above-identified application. The application corresponds to International Application WO 99/60044, filed May 19, 1999, and claims priority from German Application 192 22 468.0, filed May 19, 1988. Some changes were made in the text of the International Application to conform the enclosed Substitute Specification to US practice and to recite the invention as broadly as described. To assist the Examiner in comparing the Substitute Specification to the enclosed translation of the International Application, the following changes were made in the Substitute Specification including its claims. These changes *do not* need to be entered as an amendment to the Substitute Specification; they have already been included in the Substitute Specification and are merely shown here for the convenience of the Examiner:

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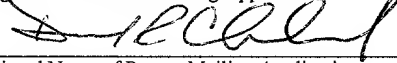
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EF285972778US

Date of Deposit

November 17, 2000

Signature of Person Mailing Application



Printed Name of Person Mailing Application

David R. Cleveland

In the Substitute Specification

At page 1, line 25, "component" was changed to --components--.

At page 2, lines 1, 5 and 6, "components" was changed to --component--.

At page 2, lines 8, 17 and 30 and page 4, lines 6, 8 and 13 (two occurrences), "dicarboxylic" was changed to --polycarboxylic--.

At page 2, line 28, "is" was changed to --can be--.

At page 3, line 7, "dicarboxylic" was changed to --polycarboxylic (e.g., dicarboxylic)--.

At page 3, lines 20 and 27; page 4, lines 2, 6, 10, 15 and 22 and page 7, line 1, the word --Preferably-- was inserted at the start of the sentences beginning on these lines.

At page 4, lines 2 and 3, "acids" was changed to --monobasic carboxylic acid--.

At page 4, lines 3, 11, 22 and 27, "more" was inserted before --preferably--.

At page 4, line 19, before "Particularly" a duplicate sentence was removed.

At page 4, line 24, "polyoxyethylene glycols of" was changed to --polyether polyols used in--.

At page 4, line 26, "used polyglycols" was changed to --polyether polyols--.

At page 5, line 1, "monocarboxylic" was changed to --monobasic carboxylic--.

At page 5, lines 2, 5 and 6, "polyalcohols" was changed to --polyvalent alcohol--.

At page 5, line 10, "means of a method" was changed to --a method--.

At page 5, line 19, "pre-reacted" was changed to --pre-cured--.

At page 5, line 23, "means of pre-curing" was changed to --pre-reacting--.

At page 7, line 5, "means of" was changed to --employing--.

At page 7, line 11, "pre-curing" was changed to --pre-reacting--.

At page 7, line 17, "patents" was changed to --patents or patent applications--.

In the Claims

The claims have been amended in the Substitute Specification as follows:

1. Two-component water paint system comprising [a] an isocyanate as the first component and an aqueous emulsion of a hydroxy-functional alkyd resin[, characterized in that] as the second component, wherein the alkyd resin can be obtained from an oleic or fatty acid component, a polyvalent alcohol, a polyether polyol having a molecular weight of 400 to 8,000, a monobasic carboxylic acid and a [dicarboxylic] polycarboxylic acid or the anhydride thereof.

2. Two-component water paint system according to claim 1, [characterized in that] wherein the hydroxy-functional alkyd resin has a hydroxyl content of 1 to 8 wt.-%.
3. Two-component water paint system according to claim 1 or 2, [characterized in that] wherein the hydroxy-functional alkyd resin is additionally modified [due to a] by reaction with isocyanate.
4. Process for the [production] preparation of a two-component water paint system according to [any of claims 1 to 3] claim 1, comprising the steps of:
 - 1) providing an isocyanate as the first component,
 - 2) preparing an aqueous emulsion of a hydroxy-functional alkyd resin comprising:
 - a) reacting an oleic or fatty acid component, a polyvalent alcohol, a polyether polyol having a molecular weight of 400 to 8,000, a monobasic carboxylic acid and a [dicarboxylic] polycarboxylic acid or the anhydride thereof to obtain a hydroxy-functional alkyd resin,
 - b) neutralizing the hydroxy-functional alkyd resin with ammonia or amine,
 - c) emulsifying the hydroxy-functional alkyd resin in water to provide the second component.
5. Process according to claim 4, [characterized in that] wherein the hydroxy-functional alkyd resin has a hydroxyl content of 1 to 8 wt.-%.
6. Process according to claim 4, wherein the alkyd resin is additionally reacted with isocyanate.
7. Process for painting a substrate using a paint system prepared according to claim 4, comprising the steps of mixing the first and second components shortly before painting and applying the resulting mixture to the substrate.
8. Process according to claim 7, wherein the paint is applied in a film having a thickness of at least 120 μm .
9. A painted article comprising a substrate coated with an essentially bubble-free film comprising a cured paint system according to claim 1.

10. A painted article according to claim 9, wherein the film has a thickness of at least 120 μm .

REMARKS

In addition to the changes shown above, the first sentence of the Abstract has been reworded slightly, and several spelling and punctuation corrections have been made in the Substitute Specification. These changes have not been identified herein but can be identified in detail if desired by the Examiner.

These amendments in the Substitute Specification are mainly editorial in nature and are made in the interest of conforming the specification and its terminology to US practice. The amendments are supported in the International Application and do not enlarge the scope of the claimed invention. The recited polycarboxylic acids are supported at, for example, page 7, line 11 of the International Application. The use of the phrases "preferably" and "more preferably" at various parts of the Substitute Specification conforms the disclosure to correspond to the invention recited at, for example, page 3, lines 9 – 23 and page 7, line 11 of the International Application.

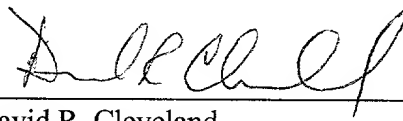
The claims have been reworded to conform them to US practice, remove multiple dependency and to add dependent claims to a process for painting and to painted articles. The claims in the Substitute Specification are fully supported in the International Application.

Favorable examination and allowance are respectfully requested.

Respectfully submitted,

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17 November 2010
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Alkyd Resin Emulsions And Uses Thereof

5 The present invention relates to a two-component water paint system and a process for its production.

 In conventional aqueous two-component polyurethane paints, CO₂ is formed in the side reaction of the isocyanate with water which leads to the undesired formation of bubbles in the paint film. According to the presently known prior art, such systems allow the reliable
10 production of layer thicknesses of at most 60 – 80 µm, depending on the degree of pigmentation and the drying conditions. The two-component water paint system of the present invention on the other hand is especially characterized by low degree of bubble formation. This allows the production of layers having a thickness of at least 120 µm, often at least 150 µm without any undesired bubble formation.

15 Due to ecological problems and the resulting necessity of reducing solvent emissions, water-dilutable paints have been widely used and in many fields of application replaced solvent-containing paints and coatings.

 For years, aqueous two-component polyurethane systems have proved to be worthwhile in those fields of application which require a high degree to weathering resistance, corrosion control and chemical resistance. These two-component systems comprise a polyol component and an isocyanate component which are mixed shortly before processing. Usually, oligomeric polyisocyanates, e.g., on the basis of hexamethylene diisocyanate and isophorone diisocyanate, are used as isocyanate components. Hydroxy-functional polyacrylate primary and secondary
20 dispersions, water-soluble or water-emulsifiable polyester and hydroxy-functional polyurethane dispersions are primarily used as polyol components.

25 These paint systems are increasingly used, e.g., as automotive paints and as lacquers for plastics and furniture. In many cases, the problem of unreliability of the process prevented a more widespread application. In particular, in the case of high layer thicknesses and unfavorable climatic conditions such as, e.g., high humidity, a strong formation of bubbles takes place due to
30 the CO₂ formed in the side reaction of the isocyanate with water during drying.

The object underlying the present invention is to provide a two-component water paint system showing only a low tendency to form bubbles and suitable for producing bubble-free paint layers having a thickness of at least 120 μm , preferably at least 150 μm .

This object is achieved by a two-component water paint system comprising an isocyanate component and an aqueous emulsion of a hydroxy-functional alkyd resin. The hydroxy-functional alkyd resin can be obtained from an oleic or fatty acid component, a polyvalent alcohol, a polyether polyol having a molecular weight of 400 to 8,000, a monobasic carboxylic acid and a polycarboxylic acid or the anhydride thereof.

The water paints of the present invention are suitable to be applied to different substrates such as, e.g., plastic materials, metal and wood.

Furthermore, the invention provides a process for the production of the inventive two-component water paint system, comprising:

- 1) providing an isocyanate component,
- 2) preparing an aqueous emulsion of a hydroxy-functional alkyd resin comprising:
 - a) reacting an oleic or fatty acid component, a polyvalent alcohol, a polyether polyol having a molecular weight of 400 to 8,000, a monobasic carboxylic acid and a polycarboxylic acid or the anhydride thereof to obtain a hydroxy-functional alkyd resin,
 - b) neutralizing the alkyd resin with ammonia or amine,
 - c) emulsifying the alkyd resin in water.

Similar alkyd resin emulsions are, in principle, already described, e.g., in US-A-3,442,835; however, they have been exclusively employed as binding agents in air-drying or baking single-component paints. Single-component paints essentially differ from two-component paints in their level of quality. Two-component polyurethane paints are clearly superior to alkyd-based air-drying single-component paints in terms of mechanical properties such as flexibility and hardness but also with respect to weathering resistance, and resistance to solvents and environmental exposure (cf. *Farbe & Lack*, 2/98, page 85).

The alkyd resin of the present invention can be prepared from an oleic or fatty acid component, a polyvalent alcohol, a polyether polyol having a molecular weight of 400 to 8,000, a monobasic carboxylic acid and a polycarboxylic acid or the anhydride thereof.

Preferably, the alkyd resin comprises 10 to 70 wt.-%, particularly preferred 15 to 40 wt.-%, of an oleic or fatty acid component, 10 to 35 wt.-%, particularly preferred 10 to 30 wt.-%, of a polyvalent alcohol having 2 to 6 hydroxyl groups, 3 to 15 wt.-%, particularly preferred 3 to 8 wt.-%, of a polyether polyol having a molecular weight of 400 to 8,000, in particular 1,000 to 6,000, 0 to 25 wt.-%, particularly preferred 10 to 20 wt.-%, of a monobasic carboxylic acid having 6 to 18 carbon atoms, and 10 to 35 wt.-%, particularly preferred 15 to 30 wt.-%, of a polycarboxylic (e.g., a dicarboxylic) acid having 4 to 10 carbon atoms or the anhydride thereof. Optionally, up to 10 wt.-% of a polybasic carboxylic acid such as, e.g., trimellitic acid or the anhydride thereof can be present in the production of the hydroxy-functional alkyd resin.

Preferably, natural oils or their fatty acids, in particular non-drying oils or their fatty acids, which are characterized by good weathering resistance and a low tendency to yellowing, are used as oleic or fatty acid components. The non-drying oils used in the present invention include all natural oils which are usually employed in the production of alkyd resins. The term 'non-drying oil' in this connection refers to a triglyceride of fatty acids which usually have 10 to 24 carbon atoms per molecule and an iodine number of <110. Mixtures are also encompassed by the present invention.

Suitable oils include vegetable oils such as apricot kernel oil, peanut oil, kapok oil, coconut oil, almond oil, olive oil, palm oil and castor oil. Peanut oil, coconut oil and castor oil are preferred.

Preferably the amount of oil used in the present invention can vary from 10 to 70 wt.-%, more preferably 15 to 40 wt.-%, of the final product.

The term 'oils' also includes esters of fatty acids with 10 to 24 carbon atoms with triols, such as trimethylolethane and trimethylolpropane, wherein the molar ratio of fatty acid to triol is 3:1. According to the present invention, the oils can be employed as such or as ester-forming precursors such as fatty acids and triols, wherein the ester is formed *in situ*. Furthermore, mixtures of different oils can be used as oleic or fatty acid components.

Preferably the monobasic carboxylic acid used in the present invention has 6 to 18 carbon atoms per molecule and includes saturated aliphatic acids, saturated cycloaliphatic acids and aromatic acids. Typical examples include isodecanoic acid, isooctanoic acid, cyclohexanoic acid, cyclopentanoic acid, benzoic acid, p-tert.-butylbenzoic acid and long-chain fatty acids derived from substances like coconut oil, palm kernel oil, babassu oil and other fats and oils

known in the technical field. Mixtures of these acids can be used as well. Preferably, benzoic acid and p-tert.-butylbenzoic acid are used. Preferably the amount of the monobasic carboxylic acid used in the present invention is about 0 to about 25 wt.-%, more preferably about 10 to about 20 wt.-%, of the alkyd resin. Mixtures of the monobasic carboxylic acids are also encompassed by the present invention.

Preferably the polycarboxylic acids used in the present invention and their anhydrides have 4 to 10 carbon atoms per molecule and include aliphatic, cycloaliphatic and aromatic polycarboxylic acids and their anhydrides. Examples of these acids or anhydrides include maleic acid, fumaric acid, terephthalic acid, isophthalic acid, adipic acid, glutaric acid, azelaic acid and phthalic acid or the anhydrides of these compounds. Preferably the amounts thereof used in the present invention are about 10 to about 35 wt.-%, more preferably about 15 to about 30 wt.-%, of the alkyd resin. Especially preferred are phthalic acid, isophthalic acid and adipic acid as polycarboxylic acid or anhydride. Mixtures of the polycarboxylic acids or their anhydrides are also encompassed by the present invention.

Preferably the polyvalent alcohols used in the present invention have at least 2, however, not more than 6, hydroxy groups per molecule and 2 to 8 carbon atoms. Examples of these polyvalent alcohols include ethylene glycol, diethylene glycol, glycerine, trimethylolethane, trimethylolpropane, pentaerythritol, dipentaerythritol, sorbitol, mannitol and similar polyvalent alcohols which can be used for the preparation of alkyd resins. Particularly preferred polyvalent alcohols are glycerine, pentaerythritol and trimethylolpropane. Mixtures of polyvalent alcohols are encompassed by the present invention.

Preferably in order to increase emulsifiability, about 3 to about 15 wt.-%, more preferably about 3 to about 8 wt.-%, of polyether polyols such as polyethylene glycol, polypropylene glycol or polytetrahydrofuran are incorporated in the alkyd resin. Preferably, the polyether polyols used in the present invention comprise a long chain of repeating oxyethylene units with a hydroxy group at each end of the chain. The preferred average molecular weight of the polyether polyols is about 400 to about 8,000, more preferably about 1,000 to about 6,000. Mixtures of polyether polyols are also encompassed by the present invention.

As is common in alkyd resin chemistry, the alkyd resin can be prepared in a one-step or two-step process.

In the one-step process, the oleic or fatty acid component, the monobasic carboxylic acid, the polyvalent carboxylic acid or the anhydride are esterified with the polyvalent alcohol and the polyether alcohol at temperatures from 180 to 260°C until an acid number of 3 to 80 KOH/g, preferably 8 to 20 KOH/g, is reached.

5 The two-step process usually starts from the natural oil which is reacted with polyvalent alcohol at temperatures from 180 to 260°C until the desired degree of transesterification is reached. In the second step, this reaction product is esterified with the mono and polycarboxylic acids and the polyether alcohol at 200°C to 260°C, while water is eliminated, until an acid number of 3 to 80 mg KOH/g, preferably 8 to 20 KOH/g, is reached. The acid number can be
10 determined by a method according to DIN 53402.

In the case that the oleic or fatty acid component is formed *in situ* from precursors, e.g., fatty acid and triol, a one-step process is preferred.

Preferably, the hydroxyl content of the inventive alkyd resin is 1 to 8 wt.-% based on the alkyd resin. Resins with a low hydroxyl content require smaller amounts of the expensive isocyanate for curing while resins with a high hydroxyl content require higher amounts of isocyanate, however, the latter exhibit a superior chemical resistance. As is common in the technical field, the hydroxyl content can be determined by reaction with acetic acid anhydride.

For increasing the initial molecular weight and for improving physical drying or accelerating initial drying the alkyd resin can be pre-reacted with isocyanates. However, during
20 the modification of the hydroxy-functional alkyd resin with isocyanate no more than 30% of the available hydroxyl groups should be reacted.

Mono-, di- or triisocyanates alone or in admixture can be used for modifying the hydroxy-functional alkyd resin by pre-reacting with isocyanate. Examples of the isocyanates used in the present invention include toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, 3-
25 phenyl-2-ethylene diisocyanate, 1,5-naphthalene diisocyanate, cumene-2,4-diisocyanate, 4-methoxy-1,3-diphenyl diisocyanate, 4-chloro-1,3-phenyldiisocyanate, diphenylmethane-4,4'-diisocyanate, diphenylmethane-2,4'-diisocyanate, diphenylmethane-2,2'-diisocyanate, 4-bromo-1,3-phenyldiisocyanate, 4-ethoxy-1,3-phenyl diisocyanate, 2,4'-diisocyanatodiphenylether, 5,6-dimethyl-1,3-phenyldiisocyanate, 2,4-dimethyl-1,3-phenyldiisocyanate, 4,4'-diiso-
30 cyanatodiphenylether, 4,6-dimethyl-1,3-phenyldiisocyanate, 9,10-anthracene diisocyanate, 2,4,6-toluene triisocyanate, 2,4,4'-triisocyanatodiphenylether, 1,4-tetramethylene diisocyanate, 1,6-

hexamethylene diisocyanate, 1,10-decamethylene diisocyanate, 1,3-cyclohexylene diisocyanate, 4,4'-methylene-bis(cyclohexyl isocyanate), xylene diisocyanate, 1-isocyanato-3-methylisocyanato-3,5,5-trimethylcyclohexane (isophorone diisocyanate), 1,3-bis(isocyanato-1-methylethyl)-benzene (m-TMXDI) and 1,4-bis(isocyanato-1-methylethyl)benzene (p-TMXDI).

5 Preferably, toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, diphenylmethane-4,4'-diisocyanate, diphenylmethane-2,4'-diisocyanate, diphenylmethane-2,2'-diisocyanate, 1,6-hexamethylene diisocyanate and isophorone diisocyanate are used in the present invention. The reaction with isocyanate usually takes place in the temperature range from 10 to 70°C, preferably 20 to 50°C.

10 After neutralization with ammonia or amines, the alkyd resins according to the present invention can be emulsified in water without the addition of solvents. The resulting emulsions usually have a solids content of 20 to 70%, preferably 30 to 55%, and a pH value of 6 to 9.

Neutralization can be achieved by adding a small amount of a neutralizing agent which neutralizes a part or all of the acid groups in the resin.

15 Suitable neutralizing agents which can be used in the present invention include ammonia, ammonium hydroxide and primary, secondary and tertiary mono- or polyamines, including hydroxylamines and in particular low alkylamines, such as ethylamine, butylamine, dimethylamine, diethylamine, dimethylethylamine, dimethylisopropylamine, diethanolamine, triethanolamine, aminopropanol, dimethylaminopropanol, tributylamine, triethylamine, 20 triisopropanolamine, ethanolamine, dimethylethanolamine or butanolamine. Amines which are volatile at temperatures below 180°C, preferably 120°C, are preferred. Especially preferred amines include ammonia, triethylamine, dimethylethylamine, dimethylisopropylamine, dimethylethanolamine, ethanolamine, diethanolamine, triethanolamine, aminopropanol and dimethylaminopropanol. The amines can be added in undiluted form wherein essentially 25 anhydrous neutralized resin products are obtained which can be diluted with water or dispersed in water basically without restrictions. Alternatively, the resins can be neutralized by the addition of an aqueous solution or dispersion of amines. Inorganic neutralizing agents such as potassium or sodium hydroxide or carbonates can be used as well. Mixtures of neutralizing agents can also be used.

Preferably the resin is then adjusted to a certain viscosity in water and an aqueous dispersion with 5 to 55 wt.-%, more preferably 25 to 55 wt.-%, resin solids (non-volatile) is obtained.

Subsequently, the described alkyd resin emulsions can then be formulated to give pigmented or unpigmented parent paints by employing additives commonly used in the paint industry, such as pigments, filler materials and auxiliary agents.

These alkyd emulsions are characterized by excellent stability in the pH range from 6 to 9 and are very suitable for formulating aqueous two-component paints.

Shortly before processing the curing agent, i.e. the isocyanate, is added to the parent paint and mixed in either manually or mechanically to give a homogeneous mixture. The compounds listed as pre-reacting agents are suitable isocyanates. However, especially suitable are oligomeric polyisocyanates as used in conventional solvent-containing two-component polyurethane paints. They include for example pre-adducts, isocyanurates, uretdiones, allophanes and the like on the basis of hexamethylene diisocyanate, isophorone diisocyanate and toluene diisocyanate. Oligomeric polyisocyanates comprising hydrophilic components which were formulated specifically for use in water paint systems are also suitable. Such isocyanate components are for example described in the patents or patent applications EP-B1-0 540 958, EP-B1-0 645 410, EP-A2-0 754 713 and EP-A1-0 697 424.

An organic solvent such as, e.g., an ester, a ketone or an alkylated ester of polyvalent alcohols or oligomeric polyglycols, such as methoxypropyl acetate, methoxydiglycol acetate or the like can be added to the isocyanate component in order to improve its incorporation or to decrease the viscosity. The amount of solvent is usually in the range of 10 to 40 wt.-%, based on the isocyanate.

The mixing ratio of parent paint and isocyanate curing agent depends on the number of hydroxyl groups in the polyol component and the NCO content in the isocyanate component. The stoichiometric ratio is calculated based on the basic isocyanate value, which defines the amount of polyisocyanate which is equivalent to 100 parts by weight of the hydroxy group containing components.

$$\text{basic isocyanate value} = \frac{42 \times 100 \times \text{OH \% in the polyol component}}{17 \times \text{NCO \% in the isocyanate component}}$$

In practice, this basic isocyanate value works as a guide value. Depending on the desired properties of the paint system, the amount of curing agent can be varied considerably. Usually, markedly higher isocyanate amounts are used in water paints since for example part of the isocyanate reacts with water to form polyureas and is then no longer available for cross-linking with the polyol component.

Depending on its composition, this mixture has a processing time from 10 minutes to 6 hours at room temperature. The paint is either cured at room temperature or under forced drying conditions like heating. The reaction can be accelerated by means of catalysts common in polyurethane chemistry, e.g. metal salts, amines and the like.

Surprisingly, the two-component water paint systems of the present invention allow the production of paint layers with a thickness of more than 120 μm and even more than 150 μm without the formation of bubbles, even under unfavorable climatic conditions such as increased humidity. Thus, high quality coatings can be produced with the systems of the present invention which match those produced with conventional solvent-containing two-component polyurethane paint, particularly as far as resistance and mechanical properties such as for example hardness, flexibility, adhesion and the like are concerned.

The following examples illustrate the invention.

Example 1

100 g peanut oil, 38 g polyethylene glycol, 78 g para-tert-butylbenzoic acid and 75 g pentaerythritol are heated at 230°C for 3 hours. Then, 126 g phthalic acid anhydride and 38 g pentaerythritol are added and the reaction mixture is esterified at temperatures of 180 to 250°C, while water is eliminated, until an acid number of 10 to 20 mg KOH/g is reached.

The reaction mixture is neutralized with triethylamine and emulsified in 550 g water. A finely divided emulsion with a solids content of about 45 wt.-% and a pH value of about 7 is obtained.

Example 2

The alkyd resin emulsion obtained in Example 1 is used to prepare a white finish according to the following formulation.

	A	33.3	parts by weight	alkyd emulsion from Example 1
	B	27.8	parts by weight	titanium dioxide
	C	0.7	parts by weight	dispersion additive
	E	26.7	parts by weight	alkyd emulsion from Example 1
5	F	8.5	parts by weight	water

The mixture of A, B and C is dispersed by means of a stirred ball mill. Then components E and F are added.

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Example 3

The parent paint prepared in Example 2 is mixed in a weight ratio of 4:1 with an isocyanate curing agent of the following composition

	70	parts by weight	polyisocyanate based on hexamethylene diisocyanate and
15	30	parts by weight	methoxypropyl acetate

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The paint/curing agent mixture has a processing time of about 4 hours and can be processed to give a dry layer thickness of up to 180 μm without any undesired formation of bubbles due to the release of CO_2 . Drying takes place overnight or in a forced manner for about 30 minutes at 80 to 100°C. Suitable substrates include, e.g., plastic materials, metal and wood.

Example 4

Clear lacquer alkyd emulsion basis as furniture or parquetry sealing

25	87 g	alkyd emulsion from Example 1
	2 g	flow-control additives
	2 g	butyldiglycol acetate and
	9 g	water

30 are mixed homogeneously.

Prior to processing, the isocyanate component of Example 2 is added in a ratio of 3:1.

The paint can be processed up to a dry layer thickness of 150 μm without the formation of bubbles. The processing time is about 4 hours. Curing time at room temperature is about 15 hours. Forced drying at about 80°C is possible.

We claim:

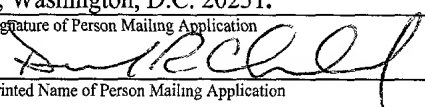
1. Two-component water paint system comprising an isocyanate as the first component and an aqueous emulsion of a hydroxy-functional alkyd resin as the second component, wherein the alkyd resin can be obtained from an oleic or fatty acid component, a polyvalent alcohol, a polyether polyol having a molecular weight of 400 to 8,000, a monobasic carboxylic acid and a polycarboxylic acid or the anhydride thereof.
2. Two-component water paint system according to claim 1, wherein the hydroxy-functional alkyd resin has a hydroxyl content of 1 to 8 wt.-%.
3. Two-component water paint system according to claim 1 or 2, wherein the hydroxy-functional alkyd resin is additionally modified by reaction with isocyanate.
4. Process for the preparation of a two-component water paint system according to claim 1, comprising the steps of:
 - 1) providing an isocyanate as the first component,
 - 2) preparing an aqueous emulsion of a hydroxy-functional alkyd resin comprising:
 - a) reacting an oleic or fatty acid component, a polyvalent alcohol, a polyether polyol having a molecular weight of 400 to 8,000, a monobasic carboxylic acid and a polycarboxylic acid or the anhydride thereof to obtain a hydroxy-functional alkyd resin,
 - b) neutralizing the hydroxy-functional alkyd resin with ammonia or amine,
 - c) emulsifying the hydroxy-functional alkyd resin in water to provide the second component.
5. Process according to claim 4, wherein the hydroxy-functional alkyd resin has a hydroxyl content of 1 to 8 wt.-%.
6. Process according to claim 4, wherein the alkyd resin is additionally reacted with isocyanate.

7. Process for painting a substrate using a paint system prepared according to claim 4, comprising the steps of mixing the first and second components shortly before painting and applying the resulting mixture to the substrate.
8. Process according to claim 7, wherein the paint is applied in a film having a thickness of at least 120 μm .
9. A painted article comprising a substrate coated with an essentially bubble-free film comprising a cured paint system according to claim 1.
10. A painted article according to claim 9, wherein the film has a thickness of at least 120 μm .

Abstract

Alkyd resin emulsions and uses thereof

A two-component water paint system that allows reliable formation of essentially bubble-free paint films having a thickness of at least 120 μm . The water paint system comprises an aqueous emulsion of a hydroxy-functional alkyd resin wherein the hydroxy-functional alkyd resin can be obtained from an oleic or fatty acid component, a polyvalent alcohol, a polyether polyol having a molecular weight of 400 to 8,000, a monobasic carboxylic acid and a polycarboxylic acid or the anhydride thereof.

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(54) Bezeichnung: ALKYDHARZEMULSIONEN UND DEREN ANWENDUNGEN			
(57) Abstract			
<p>Described is a two-component water paint system enabling process-reliable, practically bubble-free paint coatings with a thickness of at least 120 μm. The water paint system comprises an aqueous emulsion of a hydroxy-functional alkyl resin, whereby the latter can be obtained from an oleic or fatty acid component, a polyvalent alcohol, a polyether polyol having a molecular weight of 400 to 8,000, a monobasic carboxylic acid and a dicarboxylic acid or the anhydride thereof.</p>			
(57) Zusammenfassung			
<p>Beschrieben wird ein Zwei-Komponenten-Wasserlacksystem mit dem sich prozeßsicher im wesentlichen blasenfreie Lackschichten mit einer Dicke von mindestens 120 μm herstellen lassen. Das Wasserlacksystem umfaßt eine wäßrige Emulsion eines hydroxyfunktionellen Alkydharzes, wobei das hydroxyfunktionelle Alkydharz aus einer Öl- oder Fettsäurekomponente, einem mehrwertigen Alkohol, einem Polyetherpolyol mit einem Molekulargewicht von 400 bis 8000, einer einbasigen Carbonsäure und einer Dicarbonsäure bzw. deren Anhydrid erhältlich ist.</p>			

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Alkyd resin emulsions and uses thereof

The present invention relates to a two-component water paint system and a process for its production.

In conventional aqueous two-component polyurethane paints, CO₂ is formed in the side reaction of the isocyanate with water which leads to the undesired formation of bubbles in the paint film. According to the presently known prior art, such systems allow the reliable production of layer thicknesses of at most 60 – 80 μm , depending on the degree of pigmentation and the drying conditions. The two-component water paint system of the present invention on the other hand is especially characterized by low degree of bubble formation. This allows the production of layers having a thickness of at least 120 μm , often at least 150 μm without any undesired bubble formation.

Due to ecological problems and the resulting necessity of reducing solvent emissions, water-dilutable paints have been widely used and in many fields of application replaced solvent-containing paints and coatings.

For years, aqueous two-component polyurethane systems have proved to be worthwhile in those fields of application which require a high degree to weathering resistance, corrosion control and chemical resistance. These two-component systems comprise a polyol component and an isocyanate component which are mixed shortly before processing. Usually, oligomeric polyisocyanates, e.g. on the basis of hexamethylene diisocyanate and isophorone diisocyanate, are used as isocyanate components. Hydroxy-functional polyacrylate primary and secondary dispersions, water-soluble or water-emulsible polyester and hydroxy-functional polyurethane dispersions are primarily used as polyol component.

These paint systems are increasingly used e.g. as automotive paints and as lacquers for plastics and furniture. In many cases, the problem of unreliability of the process prevented a more widespread application. In particular in the case of high layer thicknesses and unfavorable climatic conditions such as e.g. high humidity, a strong formation of bubbles takes place due to the CO_2 formed in the side reaction of the isocyanate with water during drying.

The object underlying the present invention is to provide a two-components water paint system showing only a low tendency to form bubbles and suitable for producing bubble-free paint layers having a thickness of at least $120\text{ }\mu\text{m}$, preferably at least $150\text{ }\mu\text{m}$.

This object is achieved by a two-component water paint system comprising an isocyanate components and an aqueous emulsion of a hydroxy-functional alkyd resin. The hydroxy-functional alkyd resin can be obtained from an oleic or fatty acid components, a polyvalent alcohol, a polyether polyol having a molecular weight of 400 to 8,000, a monobasic carboxylic acid and a dicarboxylic acid or the anhydride thereof.

The water paints of the present invention are suitable to be applied to different substrates such as e.g. plastic materials, metal and wood.

Furthermore, the invention provides a process for the production of the inventive two-component water paint system comprising

- 1) providing an isocyanate component,
- 2) preparing an aqueous emulsion of a hydroxy-functional alkyd resin comprising:
 - a) reacting an oleic or fatty acid component, a polyvalent alcohol, a polyether polyol having a molecular weight of 400 to 8,000, a monobasic carboxylic acid and a dicarboxylic acid or the anhydride thereof to obtain a hydroxy-functional alkyd resin,
 - b) neutralizing the alkyd resin with ammonia or amine,
 - c) emulsifying the alkyd resin in water.

Similar alkyd resin emulsions are in principle already described, e.g. in US-A-3,442,835, however, they have been exclusively employed as binding agents in air-drying or baking single-component paints. Single-component paints essentially differ from two-component paints in their level of quality. Two-component polyurethane paints are clearly superior to alkyd-based air-drying single-component paints in terms of mechanical properties such as flexibility and hardness but also with respect to weathering resistance, and resistance to solvents and environmental exposure (cf. *Farbe & Lack*, 2/98, page 85).

The alkyd resin of the present invention is prepared from an oleic or fatty acid component, a polyvalent alcohol, a polyether polyol having a molecular weight of 400 to 8,000, a monobasic carboxylic acid and a dicarboxylic acid or the anhydride thereof.

Preferably, the alkyd resin comprises 10 to 70 wt.-%, particularly preferred 15 to 40 wt.-%, of an oleic or fatty acid component, 10 to 35 wt.-%, particularly preferred 10 to 30 wt.-%, of a polyvalent alcohol having 2 to 6 hydroxyl groups, 3 to 15 wt.-%, particularly preferred 3 to 8 wt.-%, of a polyether polyol having a molecular weight of 400 to 8,000, in particular 1,000 to 6,000, 0 to 25 wt.-%, particularly preferred 10 to 20 wt.-%, of a monobasic carboxylic acid having 6 to 18 carbon atoms, and 10 to 35 wt.-%, particularly preferred 15 to 30 wt.-%, of a dicarboxylic acid having 4 to 10 carbon atoms or the anhydride thereof. Optionally, up to 10 wt.-% of a polybasic

carboxylic acid such as e.g. trimellitic acid or the anhydride thereof can be present in the production of the hydroxy-functional alkyd resin.

Preferably, natural oils or their fatty acids, in particular non-drying oils or their fatty acids, which are characterized by good weathering resistance and a low tendency to yellowing, are used as oleic or fatty acid components. The non-drying oils used in the present invention include all natural oils which are usually employed in the production of alkyd resins. The term "non-drying oil" in this connection refers to a triglyceride of fatty acids which usually have 10 to 24 carbon atoms per molecule and an iodine number of <110. Mixtures are also encompassed by the present invention.

Suitable oils include vegetable oils such as apricot kernel oil, peanut oil, kapok oil, coconut oil, almond oil, olive oil, palm oil and castor oil. Peanut oil, coconut oil and castor oil are preferred.

The amount of oil used in the present invention can vary from 10 to 70 wt.-%, preferably 15 to 40 wt.-%, of the final product.

The term oils also includes esters of fatty acids with 10 to 24 carbon atoms with triols, such as trimethylolethane and trimethylolpropane, wherein the molar ratio of fatty acid to triol is 3:1. According to the present invention, the oils can be employed as such or as ester-forming precursors such as fatty acids and triols, wherein the ester is formed in situ. Furthermore, mixtures of different oils can be used as oleic or fatty acid components.

The monobasic carboxylic acid used in the present invention has 6 to 18 carbon atoms per molecule and includes saturated aliphatic acids, saturated cycloaliphatic acids and aromatic acids. Typical examples include isodecanoic acid, isooctanoic acid, cyclohexanoic acid, cyclopentanoic acid, benzoic acid, p-tert.-butylbenzoic acid and long-chain fatty acids derived from substances like coconut oil, palm kernel oil, babassu oil and other fats and oils known in the technical field. Mixtures of these acids can be used as well. Preferably, benzoic acid and p-tert.-butylbenzoic acid are used. The amount of the acids used in the present invention is about 0 to about 25

The dicarboxylic acids used in the present invention and their anhydrides have 4 to 10 carbon atoms per molecule and include aliphatic, cycloaliphatic and aromatic dicarboxylic acids and their anhydrides. Examples of these acids or anhydrides include maleic acid, fumaric acid, terephthalic acid, isophthalic acid, adipinic acid, glutaric acid, azelaic acid and phthalic acid or the anhydrides of these compounds. The amounts thereof used in the present invention are about 10 to about 35 wt.-%, preferably about 15 to about 30 wt.-%, of the alkyd resin. Especially preferred are phthalic acid, isophthalic acid and adipinic acid as dicarboxylic acid or anhydride. Mixtures of the dicarboxylic acids are also encompassed by the present invention.

In order to increase emulsibility, about 3 to about 15 wt.-%, preferably about 3 to about 8 wt.-%, of polyether polyols such as polyethylene glycol, polypropylene glycol or polytetrahydrofuran are incorporated in the alkyd resin. Preferably, the polyoxyethylene glycols of the present invention comprise a long chain of repeating oxyethylene units with a hydroxy group at each end of the chain. The preferred average molecular weight of the used polyglycols is about 400 to about 8,000, preferably about 1,000 to about 6,000. Mixtures of polyether polyols are also encompassed by the present invention.

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The two-step process usually starts from the natural oil which is reacted with polyalcohols at temperatures from 180 to 260°C until the desired degree of transesterification is reached. In the second step, this reaction product is esterified with the mono and polycarboxylic acids and the polyether alcohol at 200°C to 260°C, while water is eliminated, until an acid number of 3 to 80 mg KOH/g, preferably 8 to 20 KOH/g, is reached. The acid number can be determined by means of a method according to DIN 53402.

Preferably, the hydroxyl content of the inventive alkyd resin is 1 to 8 wt.-% based on the alkyd resin. Resins with a low hydroxyl content require smaller amounts of the expensive isocyanate for curing while resins with a high hydroxyl content require higher amounts of isocyanate, however, the latter exhibit a superior chemical resistance. As is common in the technical field, the hydroxyl content can be determined by reaction with acetic acid anhydride.

Mono-, di- or triisocyanates alone or in admixture can be used for modifying the hydroxy-functional alkyd resin by means of pre-curing with isocyanate. Examples of the isocyanates used in the present invention include toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, 3-phenyl-2-ethylene diisocyanate, 1,5-naphthalene diisocyanate, cumene-2,4-diisocyanate, 4-methoxy-1,3-diphenyl diisocyanate, 4-chloro-1,3-phenyldiisocyanate, diphenylmethane-4,4'-diisocyanate, diphenylmethane-

2,4'-diisocyanate, diphenylmethane-2,2'-diisocyanate, 4-bromo-1,3-phenyl-diisocyanate, 4-ethoxy-1,3-phenyl diisocyanate, 2,4'-diisocyanatodiphenylether, 5,6-dimethyl-1,3-phenyldiisocyanate, 2,4-dimethyl-1,3-phenyldiisocyanate, 4,4'-diisocyanatodiphenylether, 4,6-dimethyl-1,3-phenyldiisocyanate, 9,10-anthracene diisocyanate, 2,4,6-toluene triisocyanate, 2,4,4'-triisocyanatodiphenylether, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 1,10-decamethylene diisocyanate, 1,3-cyclohexylene diisocyanate, 4,4'-methylene-bis(cyclohexylisocyanate), xylenediisocyanate, 1-isocyanato-3-methylisocyanato-3,5,5-trimethylcyclohexane (isophoronediiisocyanate), 1,3-bis(isocyanato-1-methylethyl)-benzene (m-TMXDI) and 1,4-bis(isocyanato-1-methylethyl)benzene (p-TMXDI). Preferably, toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, diphenylmethane-4,4'-diisocyanate, diphenylmethane-2,4'-diisocyanate, diphenylmethane-2,2'-diisocyanate, 1,6-hexamethylene diisocyanate and isophorone diisocyanate are used in the present invention. The reaction with isocyanate usually takes place in the temperature range from 10 to 70°C, preferably 20 to 50°C.

After neutralization with ammonia or amines, the alkyd resins according to the present invention can be emulsified in water without the addition of solvents. The resulting emulsions usually have a solids content of 20 to 70%, preferably 30 to 55%, and a pH value of 6 to 9.

Neutralization can be achieved by adding a small amount of a neutralizing agent which neutralizes a part or all of the acid groups in the resin.

Suitable neutralizing agents which can be used in the present invention include ammonia, ammonium hydroxide and primary, secondary and tertiary mono- or polyamines, including hydroxyamines and in particular low alkylamines, such as ethylamine, butylamine, dimethylamine, diethylamine, dimethylethylamine, dimethylisopropylamine, diethanolamine, triethanolamine, aminopropanol, dimethylamino-propanol, tributylamine, triethylamine, triisopropanolamine, ethanolamine, dimethylethanolamine or butanolamine. Amines which are volatile at temperatures below 180°C, preferably 120°C, are preferred. Especially preferred amines include ammonia, triethylamine, dimethylethylamine, dimethylisopropylamine, dimethylethanolamine, ethanolamine, diethanolamine, triethanolamine, aminopropanol and

dimethylaminopropanol. The amines can be added in undiluted form wherein essentially anhydrous neutralized resin products are obtained which can be diluted with water or dispersed in water basically without restrictions. Alternatively, the resins can be neutralized by the addition of an aqueous solution or dispersion of amines. Inorganic neutralizing agents such as potassium or sodium hydroxide or carbonates can be used as well. Mixtures of neutralizing agents can also be used.

The resin is then adjusted to a certain viscosity in water and an aqueous dispersion with 5 to 55 wt.-%, preferably 25 to 55 wt.-%, resin solids (non-volatile) is obtained.

Subsequently, the described alkyd resin emulsions can then be formulated to give pigmented or unpigmented parent paints by means of additives commonly used in the paint industry, such as pigments, filler materials and auxiliary agents.

These alkyd emulsions are characterized by excellent stability in the pH range from 6 to 9 and are very suitable for formulating aqueous two-component paints.

Shortly before processing the curing agent, i.e. the isocyanate, is added to the parent paint and mixed in either manually or mechanically to give a homogeneous mixture. The compounds listed as pre-curing agents are suitable as isocyanate. However, especially suitable are oligomeric polyisocyanates as used in conventional solvent-containing two-component polyurethane paints. They include for example pre-adducts, isocyanurates, uretdiones, allophanes and the like on the basis of hexamethylene diisocyanate, isophorone diisocyanate and toluylene diisocyanate. Oligomeric polyisocyanates comprising hydrophilic components which were formulated specifically for the use in water paint systems are also suitable. Such isocyanate components are for example described in the patents EP-B1-0 540 958, EP-B1-0 645 410, EP-A2-0 754 713 and EP-A1-0 697 424.

An organic solvent such as e.g. an ester, a ketone or an alkylated ester of polyvalent alcohols or oligomeric polyglycols, such as methoxypropyl acetate, methoxydiglycol acetate or the like can be added to the isocyanate component in order to improve its incorporation or to decrease the viscosity. The amount of solvent is usually in the range of 10 to 40 wt.-%, based on the used isocyanate.

The mixing ratio of parent paint and isocyanate curing agent depends on the number of hydroxyl groups in the polyol component and the NCO content in the isocyanate component. The stoichiometric ratio is calculated based on the basic isocyanate value, which defines the amount of polyisocyanate which is equivalent to 100 parts by weight of the hydroxy group containing components.

$$\text{basic isocyanate value} = \frac{42 \times 100 \times \text{OH \% in the polyol component}}{17 \times \text{NCO \% in the isocyanate component}}$$

In practice, this basic isocyanate value works as a guide value. Depending on the desired properties of the paint system, the amount of curing agent can be varied considerably. Usually, markedly higher isocyanate amounts are used in water paints since for example part of the isocyanate reacts with water to form polyureas and is then no longer available for cross-linking with the polyol component.

Depending on its composition, this mixture has a processing time from 10 minutes to 6 hours at room temperature. The paint is either cured at room temperature or under forced drying conditions like heating. The reaction can be accelerated by means of catalysts common in polyurethane chemistry, e.g. metal salts, amines and the like.

Surprisingly, the two-component water paint systems of the present invention allows the production of paint layers with a thickness of more than 120 μm and even more than 150 μm without the formation of bubbles, even under unfavorable climatic conditions such as increased humidity. Thus, high quality coatings can be produced with the systems of the present invention which match those produced with conventional solvent-containing two-component polyurethane paint, particularly as far as resistance and mechanical properties such as for example hardness, flexibility, adhesion and the like are concerned.

The following examples illustrate the invention.

Example 1

100 g peanut oil, 38 g polyethylene glycol, 78 g para-tert-butylbenzoic acid and 75 g pentaerythritol are heated at 230°C for 3 hours. Then, 126 g phthalic acid anhydride and 38 g pentaerythritol are added and the reaction mixture is esterified at temperatures of 180 to 250°C, while water is eliminated, until an acid number of 10 to 20 mg KOH/g is reached.

The reaction mixture is neutralized with triethylamine and emulsified in 550 g water. A finely divided emulsion with a solids content of about 45 wt.-% and a pH value of about 7 is obtained.

Example 2

The alkyd resin emulsion obtained in Example 1 is used to prepare a white finish according to the following formulation.

A	33.3	parts by weight	alkyd emulsion from Example 1
B	27.8	parts by weight	titanium dioxide
C	0.7	parts by weight	dispersion additive
E	26.7	parts by weight	alkyd emulsion from Example 1
F	8.5	parts by weight	water

The mixture of A, B and C is dispersed by means of a stirred ball mill. Then components E and F are added.

Example 3

The parent paint prepared in Example 2 is mixed in a weight ratio of 4:1 with an isocyanate curing agent of the following composition

70	parts by weight	polyisocyanate based on hexamethylene diisocyanate and
30	parts by weight	methoxypropyl acetate

The paint/curing agent mixture has a processing time of about 4 hours and can be processed to give a dry layer thickness of up to 180 μm without any undesired formation of bubbles due to the release of CO_2 . Drying takes place overnight or in a forced manner for about 30 minutes at 80 to 100°C. Suitable substrates include e.g. plastic materials, metal and wood.

Example 4

Clear lacquer alkyd emulsion basis as furniture or parquetry sealing

- 87 g alkyd emulsion from Example 1
- 2 g flow-control additives
- 2 g butyldiglycol acetate and
- 9 g water

are mixed homogeneously.

Prior to processing, the isocyanate component of Example 2 is added in a ratio of 3:1.

The paint can be processed up to a dry layer thickness of 150 μm without the formation of bubbles. The processing time is about 4 hours. Curing time at room temperature is about 15 hours. Forced drying at about 80°C is possible.

Claims

1. Two-component water paint system comprising a isocyanate component and an aqueous emulsion of a hydroxy-functional alkyd resin, characterized in that the alkyd resin can be obtained from an oleic or fatty acid component, a polyvalent alcohol, a polyether polyol having a molecular weight of 400 to 8,000, a monobasic carboxylic acid and a dicarboxylic acid or the anhydride thereof.
2. Two-component water paint system according to claim 1, characterized in that the hydroxy-functional alkyd resin has a hydroxyl content of 1 to 8 wt.-%.
3. Two-component water paint system according to claim 1 or 2, characterized in that the hydroxy-functional alkyd resin is additionally modified due to a reaction with isocyanate.
4. Process for the production of a two-component water paint system according to any of claims 1 to 3, comprising the steps
 - 1) providing an isocyanate component,
 - 2) preparing an aqueous emulsion of a hydroxy-functional alkyd resin comprising:
 - a) reacting an oleic or fatty acid component, a polyvalent alcohol, a polyether polyol having a molecular weight of 400 to 8,000, a monobasic carboxylic acid and a dicarboxylic acid or the anhydride thereof to obtain a hydroxy-functional alkyd resin,
 - b) neutralizing the hydroxy-functional alkyd resin with ammonia or amine,
 - c) emulsifying the hydroxy-functional alkyd resin in water.
5. Process according to claim 4, characterized in that the alkyd resin is additionally reacted with isocyanate.

Abstract**Alkyd resin emulsions and uses thereof**

The invention relates to a two-component water paint system by means of which essentially bubble-free paint films having a thickness of at least 120 μm can be produced reliably. The water paint system comprises an aqueous emulsion of a hydroxy-functional alkyd resin wherein the hydroxy-functional alkyd resin can be obtained from an oleic or fatty acid component, a polyvalent alcohol, a polyether polyol having a molecular weight of 400 to 8,000, a monobasic carboxylic acid and a dicarboxylic acid or the anhydride thereof.

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Docket No. 108-C1553US

COMBINED DECLARATION, POWER OF ATTORNEY AND PETITION

As a below named inventor, I hereby declare that: (1) my residence, citizenship and address are as stated below next to my name; (2) I believe that I am the original, first, and sole inventor (if only one inventor is listed below) or a joint inventor (if more than one inventor is listed below) of the subject matter described and claimed and for which a patent is sought on the invention or discovery entitled ALKYD RESIN EMULSIONS AND USES THEREOF (the "Application"), the specification of which:

- a. ☐ is attached hereto
 b. ☒ was filed on November 17, 2000, as application serial no. 09/700,901 and as amended on (if applicable).
 c. ☐ was filed on as PCT application serial no.

(3) I have reviewed and understand the contents of the Application, including the claims, as amended by any amendment referred to above; (4) I hereby acknowledge my duty to disclose to the Patent and Trademark Office all information known to me to be material to patentability of the Application as defined in the attached copy of Title 37, Code of Federal Regulations, § 1.56, and (5) I hereby claim foreign priority benefits under Title 35, United States Code, §§ 119 and 365 of any foreign applications for patent or inventor's certificate listed below and have also identified below any foreign applications for patent or inventor's certificate having a filing date before that of the Application on the basis of which priority is claimed:

- a. ☐ no such foreign applications have been filed.
 b. ☒ foreign applications have been filed as follows:

FOREIGN APPLICATIONS, IF ANY, FOR WHICH PRIORITY IS CLAIMED UNDER 35 USC § 119			
COUNTRY	APPLICATION NUMBER	DATE OF FILING (Day, Month, Year)	DATE OF ISSUE (Day, Month, Year)
GERMANY	198 22 468.0	MAY 19, 1998	
ALL FOREIGN APPLICATIONS, IF ANY, FILED BEFORE THE PRIORITY APPLICATION			
COUNTRY	APPLICATION NUMBER	DATE OF FILING (Day, Month, Year)	DATE OF ISSUE (Day, Month, Year)

I hereby claim the benefit under Title 35, United States Code, §§ 120 and 365 of any United States and PCT international applications listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States applications in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, § 1.56(a) that occurred between the filing date of the prior applications and the national or PCT international filing date of this application.

INTERNATIONAL APPLICATION NUMBER	DATE OF FILING (day, month, year)	STATUS (patented, pending, abandoned)
PCT/DE99/01505	May 19, 1999	

I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional applications listed below:

U.S. PROVISIONAL APPLICATION NUMBER	DATE OF FILING (day, month, year)

I hereby appoint David R. Cleveland (Reg. No. 29,524) my attorney with full powers (including the powers of appointment, substitution, and revocation) to prosecute the Application and any division, continuation, continuation-in-part, reexamination, or reissue thereof, and to transact all business in the Patent and Trademark Office connected therewith. The mailing address, telephone and facsimile numbers for correspondence with my attorney is:

Attention: David R. Cleveland
David R. Cleveland, P.A.
Suite E-1324 First Nat'l Bank Bldg.
332 Minnesota Street

FOIEU 10000260

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Saint Paul, MN 55101

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I also declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the Application or any patent issuing thereon.

Wherefore, I pray for grant of Letters Patent for the invention or discovery described and claimed in the Application, and I hereby subscribe my name to the Application, and to this Declaration, Power of Attorney and Petition, on the date set forth below.

Full Name:	Peter Kuhlmann
Citizenship:	Germany
Post Office Address:	Zwingenberger Weg 46 D-42489 Wülfrath <i>DEV</i> GERMANY
Signature:	<i>Peter Kuhlmann</i>
Date:	07/15/2001

Full Name:	Reinhard Winter
Citizenship:	Germany
Post Office Address:	Maikammer 14 <i>DEV</i> D-42489 Wülfrath GERMANY
Signature:	<i>Reinhard Winter</i>
Date:	01/15/01

Full Name:	
Citizenship:	
Post Office Address:	
Signature:	
Date:	

Full Name:	
Citizenship:	
Post Office Address:	
Signature:	
Date:	

Full Name:	
Citizenship:	
Post Office Address:	
Signature:	
Date:	

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§1.56 Duty to disclose information material to patentability.

(a) A patent by its very nature is affected with a public interest. The public interest is best served, and the most effective patent examination occurs when, at the time an application is being examined, the Office is aware of and evaluates the teachings of all information material to patentability. Each individual associated with the filing and prosecution of a patent application has a duty of candor and good faith in dealing with the Office, which includes a duty to disclose to the Office all information known to that individual to be material to patentability as defined in this section. The duty to disclose information exists with respect to each pending claim until the claim is cancelled or withdrawn from consideration, or the application becomes abandoned. Information material to the patentability of a claim that is cancelled or withdrawn from consideration need not be submitted if the information is not material to the patentability of any claim remaining under consideration in the application. There is no duty to submit information which is not material to the patentability of any existing claim. The duty to disclose all information known to be material to patentability is deemed to be satisfied if all information known to be material to patentability of any claim issued in a patent was cited by the Office or submitted to the Office in the manner prescribed by §§ 1.97(b)-(d) and 1.98. However, no patent will be granted on an application in connection with which fraud on the Office was practiced or attempted or the duty of disclosure was violated through bad faith or intentional misconduct. The Office encourages applicants to carefully examine:

- (1) prior art cited in search reports of a foreign patent office in a counterpart application, and
- (2) the closest information over which individuals associated with the filing or prosecution of a patent application believe any pending claim patentably defines, to make sure that any material information contained therein is disclosed to the Office.

(b) Under this section, information is material to patentability when it is not cumulative to information already of record or being made of record in the application, and

- (1) It establishes, by itself or in combination with other information, a prima facie case of unpatentability of a claim; or
- (2) It refutes, or is inconsistent with, a position the applicant takes in:
 - (i) Opposing an argument of unpatentability relied on by the Office, or
 - (ii) Asserting an argument of patentability.

A prima facie case of unpatentability is established when the information compels a conclusion that a claim is unpatentable under the preponderance of evidence, burden-of-proof standard, giving each term in the claim its broadest reasonable construction consistent with the specification, and before any consideration is given to evidence which may be submitted in an attempt to establish a contrary conclusion of patentability.

(c) Individuals associated with the filing or prosecution of a patent application within the meaning of this section are:

- (1) Each inventor named in the application;
- (2) Each attorney or agent who prepares or prosecutes the application; and
- (3) Every other person who is substantively involved in the preparation or prosecution of the application and who is associated with the inventor, with the assignee or with anyone to whom there is an obligation to assign the application.

(d) Individuals other than the attorney, agent or inventor may comply with this section by disclosing information to the attorney, agent, or inventor.

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